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**THE EFFECTS OF SURFACE CONDITION
ON THE CORROSION OF CANDIDATE
STRUCTURAL MATERIALS IN A SIMULATED
HTGR-GT ENVIRONMENT**

by **MASTER**
L. D. THOMPSON

**Prepared under
Contract DE-AT03-76ET35300
for the San Francisco Operations Office
Department of Energy**

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GENERAL ATOMIC COMPANY

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ABSTRACT

A simulated high-temperature gas-cooled reactor (HTGR) helium environment has been used to study the effects of surface finish conditions on the subsequent elevated-temperature corrosion behavior of key candidate structural materials. The environment contained helium with 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O at 900°C with total test exposure durations of 3000 hours. Specimens with lapped, grit-blasted, pickled, and preoxidized surface conditions were studied. Materials tested included two cast superalloys, IN 100 and IN 713LC; one centrifugally cast high-temperature alloy, HK 40; one oxide-dispersion-strengthened alloy, Inconel MA 754; and three wrought high-temperature alloys, Hastelloy Alloy X, Inconel Alloy 617, and Alloy 800H.

This environment is known to be oxidizing, as well as carburizing, with the nature and the degree of attack being dependent upon alloy chemistry. The most serious corrosion mechanism is carburization resulting in the enhanced precipitation of metal carbides both intergranularly and intragranularly. Variations in corrosion behavior were noted with the different surface finishes. However, the predominant observation was that preoxidation treatments at 900°C in air were effective in controlling the carburization of the two wrought alloys, Hastelloy X and Alloy 800H. The protective nature of the oxide surface scales for these two materials in the preoxidized condition was studied and is believed to be related to the composition and formation characteristics of these scales.

Only modest differences in corrosion behavior were observed for the pickled, lapped, and grit-blasted specimens. This indicates that the corrosion kinetics are controlled by the availability of reactant gaseous impurities as opposed to the mobility and near-surface activity of reactant solute constituents, such as chromium.

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1. INTRODUCTION

It is currently well known that the practical limitations to impurity control in high-temperature gas-cooled reactor (HTGR) helium coolant gas lead to a coolant that contains small but measureable concentrations of oxidizing and carburizing impurity species (Refs. 1-5). While the utilization of helium as a coolant provides several key advantages over other coolants (Ref. 6), the presence of these impurities makes a thorough understanding of their effects on the system a necessity.

The impurities include CO, CO₂, CH₄, H₂, and H₂O. The effects of these impurities are being studied in numerous corrosion programs, both at General Atomic Company (GA) (Ref. 1) and at other laboratories (Refs. 7, 8). The interactions of these impurities and candidate metallic structural materials indicate that carburization is the most serious corrosion mechanism. The maximum operating temperature of HTGR components may be limited by alloy carburization and the associated degradation in mechanical properties.

Carburization leads to the near-surface precipitation of intergranular and intragranular carbides, which results in substantial reductions in creep and short-time tensile ductilities for some of the candidate alloys (Refs. 1-3, 9). In addition, the depletion of solid solution strengthening solute species through these precipitation reactions can affect creep strength and reduce creep lifetimes.

Surface finish has been shown to be an important parameter in the high-temperature corrosion of alloys in other industrial applications (Refs. 10, 11). Enhancement of corrosion resistance can be achieved with proper control of the initial surface, which affects diffusion rates, elemental constituent activities, and near-surface chemical composition.

These factors influence the kinetics by which reactions can occur. Another common practice in controlling elevated-temperature corrosion is to utilize coatings, thereby either reducing or eliminating environment-substrate interactions.

This report describes the effects of prior surface treatment on the subsequent controlled-impurity helium corrosion observed for several key candidate alloys. Another report, which will be prepared at a later date, will cover the effects of various machined and ground surface conditions. The alloys tested include cast superalloys, a centrifugally cast high-temperature alloy, an oxide-dispersion-strengthened alloy, and several wrought high-temperature alloys.

2. EXPERIMENTAL PROCEDURE

Table 1 shows the test matrix that was adopted to study surface finish condition effects in a simulated gas turbine (GT) HTGR environment. Included are typical industrial practices such as pickling and grit-blasting, as well as finish preparation techniques that may appear to be more laboratory related, e.g., lapping. Also included are preoxidation treatments in air, which result in the formation of oxide surface scales and can be viewed as a simplistic coating application procedure. This report presents the results of the Phase I, Run 1 exposures.

2.1. TEST SPECIMENS

Test alloy selection was made to include promising alloy systems from various categories of presently available commercial materials. In the as-cast forms there are two cast superalloys (IN 100 and IN 713LC) and one centrifugally cast high-temperature alloy (HK 40). Three wrought high-temperature alloys (Alloy 800H, Inconel Alloy 617, and Hastelloy Alloy X), representing widely used tubing and piping materials, were also included. Finally, an iron-base oxide-dispersion-strengthened material (Inconel MA 754) was also tested. Table 2 gives the chemical compositions, heat numbers, and as-received conditions of the materials tested. In the case of HK 40, a remnant piece of cast tube was used to machine specimens and it was not possible to determine the heat number; therefore, the GA code number of the heat is given instead.

Figures 1 through 7 show the typical microstructures observed in the test alloys. Both longitudinal and transverse sections are shown to illustrate important microstructural characteristics and the effects of processing on the texture observed in the materials.

TABLE 1
TEST MATRIX - EFFECTS OF SURFACE TREATMENT ON THE CORROSION
OF STRUCTURAL MATERIALS IN A SIMULATED HTGR-GT ENVIRONMENT^(a)
PHASE 1 - RUN 1 (900°C, 3000 h)

	Cast Superalloys		Centrifugally Cast Alloy	Wrought Alloys			Y ₂ O ₃ Dispersed MA 754
	IN 100	IN 713LC	HK 40	Alloy 800H	Hast. X	Inc. 617	
Preoxidized in air at 900°C							
100 h	X	X	X	X	X	X	X
10 h	X	X	X	X	X	X	X
1 h	X	X	X	X	X	X	X
Lapped, 25.4-12.7 µcm (10-5 µin.)	X	X	X	X	X	X	X
Grit-blasted	X	X	X	X	X	X	
Pickled				X	X	X	X

^(a) He/500 µatm H₂/50 µatm CO/50 µatm CH₄/ <0.5 µatm H₂O.

TABLE 2
CHEMICAL COMPOSITION OF TEST ALLOY SYSTEMS (VENDOR VALUES)

Alloy (Heat) As-Received Condition	Composition (wt %)																			
	C	Ni	Fe	Cr	Mn	Si	Mo	Co	W	Nb	Ta	Al	Ti	Cu	V	Zr	B	P	S	Y ₂ O ₃
Hastelloy Alloy X (126007437) Solution-annealed	0.07	Bal.	18.97	22.06	0.6	0.44	8.79	1.69	0.67	--	--	--	--	--	--	--	0.002	0.02	<0.002	--
Inconel Alloy 617 (XX14A6UK) Solution-annealed	0.06	55.13	0.53	21.74	0.02	0.10	8.91	12.32	--	--	--	1.11	0.30	0.11	--	--	0.003	--	0.002	--
Alloy 800H (HH8099A) Solution-annealed	0.07	32.03	45.50	19.79	1.00	0.18	--	--	--	--	--	0.38	0.45	0.60	--	--	--	--	0.003	--
HK 40 (GA321) (a) As centrifugally cast	0.41	20.1	Bal.	25.3	0.33	1.23	--	--	--	--	--	--	--	--	--	--	--	--	--	--
IN 100 (UA0457111047) As-cast	0.18	Bal.	0.20	9.85	<0.10	<0.10	3.03	15.18	--	--	--	5.46	4.19	--	1.05	0.07	0.015	--	0.0016	--
IN 713LC (WA39856E6965) As-cast	0.06	Bal.	0.15	12.00	<0.10	<0.10	4.10	0.10	--	2.04 (Nb+Ta)		5.85	0.71	<0.10	--	0.06	0.007	0.002	0.0015	--
Inconel MA 754 (DT02A3E1-2) Mechanically alloyed	0.07	76.11	1.52	20.68	--	--	--	--	--	--	--	0.30	0.40	--	--	--	--	--	0.003	0.58

(a) General Atomic code number.

Fig. 1. Typical microstructure observed in Alloy 800H, heat HH8099A:
(a) transverse, (b, c) longitudinal

Fig. 2. Typical microstructure observed in Hastelloy X, heat 1260074737:
(a, c) transverse, (b) longitudinal

Fig. 3. Typical microstructure observed in Inconel 617, heat XX14A6UK:
(a, c) transverse, (b) longitudinal

Fig. 4. Typical microstructure observed in IN 100, heat UA45 (711047):
(a, c) longitudinal, (b) transverse

Fig. 5. Typical microstructure observed in IN 713LC, heat WA398 (66B6965):
(a) transverse, (b,c) longitudinal

Fig. 6. Typical microstructure observed in HK 40, heat GA321: (a) transverse, (b, c) longitudinal

Fig. 7. Typical microstructure observed in MA 754, heat
DTO 2A8 B1-2: (a) transverse, (b, c) longitudinal

In Figs. 1 through 3, the microstructures of the wrought high-temperature alloys show virtually no texture effect between the longitudinal and transverse sections. This is generally true of wrought materials and is associated with the solution-annealing processing step (following any mechanical rolling), which tends to produce an equiaxed microstructure. Figure 1 shows the typical solution-annealed microstructure for Alloy 800H with blocky titanium carbonitride and finer $M_{23}C_6$ carbide precipitates (Ref. 12) and having a grain size in the range of 200 to 400 μm . In Fig. 2 the microstructure of Hastelloy X is shown to be much finer grained (30 to 150 μm) with carbide stringers present throughout the microstructure. These carbides have been determined to be M_6C variants and are generally of a smaller lattice parameter than the M_6C' carbides that form with thermal aging (Refs. 9, 13, 14). Figure 3 shows the microstructure of Inconel 617, which tends to be of a larger grain size (200 to 400 μm) and in this heat is heavily twinned. Similar to Alloy 800H, Inconel 617 contains carbonitrides and $M_{23}C_6$ carbides in the solution-annealed condition.

Figures 4 and 5 show the microstructures observed for the cast superalloys IN 100 and IN 713LC, respectively. Typical of these materials, dendritic structures with a heavy density of $\text{Ni}_3(\text{Al},\text{Ti})$ precipitates were observed (Ref. 15). Also apparent is the higher density of casting defects, i.e., shrinkage pores, present in this casting of IN 100 in comparison with the IN 713LC. The microstructures in these cases represent the as-cast condition for these materials.

Figure 6 shows the as-cast microstructure of HK 40, a centrifugally cast high-temperature alloy. The high carbon concentration (~ 0.41 wt %) in the alloy leads to the grain-boundary and interdendritic precipitation of primary eutectic carbides upon solidification (Ref. 16).

Figure 7 shows the microstructure of the oxide-dispersion-strengthened nickel-base alloy, MA 754. In this case, the base alloy, which is essentially 80 Ni - 20 Cr, is mechanically alloyed with yttria dispersoids, leading to a heavily textured microstructure and a dramatic difference in longitudinal and transverse mechanical behavior (Ref. 17).

2.2. SURFACE PREPARATION

The specimens to be exposed in the simulated HTGR-GT environment were carefully prepared to give surfaces typical of the following treatments: (1) lapping, (2) pickling, (3) grit-blasting, and (4) preoxidizing. The methodology used to prepare the specimens was always that which was most consistent with laboratory or industrial practices, depending upon the specific treatment.

All corrosion test specimens were in the form of 6.35-mm (0.25-in.) diameter by 25.4-mm (1.00-in.) long cylinders with a centrally located 3.17-mm (0.125-in.) diameter hole drilled near one end for positioning in the specimen holder.

Specimens of the cast superalloys, IN 100 and IN 713LC, were sliced from 6.35-mm (0.25-in.) diameter by 76.2-mm (3.00-in.) long as-cast bars. These specimens were grit-blasted at the foundry with 90 to 120 mesh alumina, which is typical of cast turbine components. Surface preparation of these two alloys was performed with the specimens in the grit-blasted initial condition.

The wrought, oxide-dispersion-strengthened, and centrifugally cast alloy specimens were machined from bar stock, flat stock, and longitudinally cut blanks, respectively, resulting in a uniform surface finish of 8 to 16 rms. Any surface preparation for these alloys was performed with the specimen in this initial condition.

Lapping was performed by mounting the end of the specimen in an electric drill and polishing with a canvas cloth and 3- μ m diamond paste. This procedure produced specimens with a consistent finish regardless of specimen composition. Figure 8 shows a typical lapped surface, with only very fine scratches present.

The pickling procedure used involved a two-step treatment similar to that employed in many steel mills. The specimens were descaled using

Fig. 8. Scanning electron micrograph showing typical surface condition for all alloys (HK 40 shown) following a lapping treatment

the procedure listed below.

2-h immersion at 82°C (180°F) in a solution consisting of:

Potassium permanganate: 3% by volume

Sodium hydroxide: 18% by volume

Balance H₂O

Following the descaling treatment, the specimens were pickled using the procedure listed below.

20-min immersion at 60°C (140°F) in a solution consisting of:

Nitric acid: 15% by volume

Hydrofluoric acid: 2% by volume

Balance H₂O

The cast materials were not pickled since this particular procedure is not applicable to these materials. The pickling treatment produced finishes that were dependent upon alloy chemistry, since the solution reactivity depended on the alloy composition. Figure 9 shows the surfaces produced on the wrought alloys. Alloy 800H tended to etch, whereas Hastelloy X was more immune and attack was enhanced at M₆C/matrix interfaces leaving holes on the surface where carbides fell out as the surrounding matrix dissolved. Inconel 617 was even more resistant to attack, as shown in Fig. 9c. Figure 10 shows the surface produced on MA 754, where orientational effects can be noted. In Fig. 10a, the areas where preferential attack occurred are pitted in comparison with adjacent areas where little chemical attack is apparent. Figure 10b shows an area where attack was pronounced. Again the attack was greatest at particle/matrix interfaces, in this case at the interfaces of the yttria dispersoids and the alloy matrix. A close examination reveals some of the yttria particles although they are very small relative to the "holes" at the surface.

Grit-blasting was performed on all specimens using either 100 or 220 mesh alumina grit. Figure 11 shows the two types of grit used for this purpose. Surfaces of all grit-blasted test specimens were quite uniform and very similar; typical examples are shown in Fig. 12. It is

(a)

(b)

(c)

40 μm

Fig. 9. Scanning electron micrographs showing the surface conditions after pickling treatments in a HNO_3/HF solution for (a) Alloy 800H, (b) Hastelloy X, and (c) Inconel 617

(a)

40 μm

(b)

4 μm

Fig. 10. Scanning electron micrographs showing the surface condition of MA 754 following a pickling treatment in a HNO_3/HF solution

Fig. 11. Scanning electron micrographs showing the alumina grit used to perform the grit-blasting of test specimens: (a) No. 220 grit and (b) No. 100 grit

(a)

200 μm

(b)

20 μm

Fig. 12. Scanning electron micrographs showing typical surface following a grit-blasting treatment on (a) HK 40 and (b) IN 713LC

obvious from Fig. 12b that this treatment introduces a great deal of plastic deformation in a near-surface zone of the specimens. It would be expected that diffusion coefficients and possibly the activities of reactive chemical constituents, e.g., Cr, might be affected in this near-surface layer where defect densities were increased.

Preoxidation treatments were also performed at 900°C in still air for times of 1, 10, and 100 h. The resultant oxide films were intended to inhibit carburization in the subsequent controlled-impurity helium exposure. It is important to note that oxides formed in air, where the oxygen activity is very high, might not necessarily be the thermodynamically stable form of oxide that would naturally form in the simulated HTGR-GT environment. Any carburization barrier that would be formed in air would gradually (depending on kinetics) change to the stable form corresponding to the actual reactor environment as service exposure continued. Figures 13 through 16 show the preoxidized surfaces representative of the range of test specimens.

Figure 13a is representative of the oxides formed on the wrought alloys. The growth of the oxide was primarily columnar, growing out from the surface, once impingement of the nuclei occurred. In Fig 13b oxide spallation occurred on an Alloy 800H specimen, probably because of the interfacial stresses at the oxide-metal interface and stresses resulting from any mismatch in oxide and metal coefficients of thermal expansion that would be established upon cooling of the specimen from the pre-oxidation temperature.

Figure 14 shows the stages of oxidation in IN 100 with exposure times of 1, 10, and 100 h. Similar results were obtained for IN 713LC.

Figure 15 shows the oxides formed on HK 40 after a 100-h treatment. Three stages of oxide formation are apparent. The first stage involved the formation of a discontinuous silicon-rich oxide phase and was complete after only 1 h of exposure. As the exposure time increased, a patchy chromium-rich oxide formed, which gradually covered the surface to the extent shown in Fig. 15a. A close examination of Fig. 15b shows a third

(a)

(b)

20 μm

Fig. 13. Scanning electron micrographs showing the surfaces of (a) Inconel 617 and (b) Alloy 800H following preoxidation treatments at 900°C in air for 100 h. Arrow indicates a region where spallation of the oxide film has occurred.

(a)

(b)

(c)

20 μm

Fig. 14. Scanning electron micrographs showing the surface of IN 100 following preoxidation treatments in air at 900°C for (a) 1 h, (b) 10 h, and (c) 100 h

Fig. 15. Scanning electron micrographs showing the surface condition of HK 40 following a 100-h preoxidation treatment at 900°C in air

(a)

(b)

(c)

20 μm

Fig. 16. Scanning electron micrographs showing the surface of MA 754 following preoxidation treatments in air at 900°C for (a) 1 h, (b) 10 h, and (c) 100 h

phase (presumably an oxide), which nucleated on the patchy chromium-oxide areas. Longer-term exposures would be necessary to bring the oxide formation reactions to a stable or metastable condition.

Figure 16 shows the stages of oxide growth on MA 754 as a function of exposure time. The chromium-rich oxide nucleated preferentially on the yttria particles very near to the surface creating many small oxide nodules. As the exposure time increased these nodules coarsened and eventually coalesced, forming a thin oxide surface layer.

2.3. CONTROLLED-IMPURITY HELIUM EXPOSURE

The specimens were exposed isothermally at 900°C (1652°F) for 3000 h with interruptions at 500, 1000, 2000, and 3000 h for weight change measurements. Exposures were conducted in a simulated HTGR-GT environment consisting of helium containing constant concentrations of 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / $<0.5 \mu\text{atm H}_2\text{O}$.

A schematic diagram of the once-through controlled-impurity helium supply system used to generate each desired helium environment is shown in Fig. 17. Bottled high-purity nuclear-grade helium was further purified by passing it through a 5 Å molecular sieve and activated charcoal trap at liquid nitrogen temperature [-196°C (-321°F)]. Controlled quantities of H_2 , CO , and CH_4 were added by metering research-purity gases into the purified helium stream. Each controlled-impurity helium mixture was then introduced into a high-temperature retort and exhausted to atmosphere. No intentional addition of H_2O was made in the present experiments.

An overriding consideration in the design of the test system was the minimization of impurity depletion in the retorts so that gas of known and constant composition would be available to react with all specimens during exposure. Specimens were contained in alumina sample holders and exposed in 70-mm (2.75-in.) i.d. by 910-mm (36-in.) long, single-ended alumina retorts, using an alumina gas inlet tube in order to eliminate

Fig. 17. Schematic diagram of environment control system for parametric helium impurity corrosion study

reactive metal surfaces other than the specimens themselves. In addition to these precautions, flow rates through each retort were maintained at $1000 \text{ cm}^3/\text{min}$ to further minimize changes in gas composition from inlet to outlet. The impure helium gas mixtures in the retorts were maintained at positive (1.67 atm) pressure to minimize the possibility of air leaks into the test system. Heating of the retorts was accomplished using three-zone Lindberg horizontal tube furnaces with a 610-mm (24-in.) hot zone. The test zone was 75 mm (3 in.) long and contained three equally spaced monitoring thermocouples along its length. The center thermocouple was used for furnace control. Temperature in the test zone was maintained to within $\pm 5^\circ\text{C}$ ($\pm 9^\circ\text{F}$).

Test monitoring instrumentation included a Carle Model III H (S series) automatic gas chromatograph for determination of H_2 , CO, CO_2 , and CH_4 partial pressures; an EG&G Model 440 extended-range dew point hygrometer for the determination of H_2O partial pressure; and a modified Thermox zirconia cell oxygen probe for the qualitative determination of O_2 partial pressure. The helium composition in and out of each retort was measured at least once weekly, and H_2 , CO, and CH_4 levels were maintained to within $\pm 10\%$ of nominal.

2.4. TEST PROCEDURE

Exposure of the specimens was interrupted at 500, 1000, 2000, and 3000 h for visual examination and weight change measurements. Specimens were removed after 3000-h exposures for destructive analyses. All corrosion specimens removed from testing were cut perpendicular to their longitudinal axis to obtain sections for metallography, bulk carbon analysis, and surface studies.

Metallography of etched and unetched sections was performed to study surface corrosion scales, internal oxidation, carburization, and thermal aging effects. Mean oxidation and carburization depths were both measured by taking the average of eight metallographic measurements around the specimen cross section.

Alloy phases and the compositions of surface scales were identified by scanning electron microscope (SEM) microprobe analysis, including selected area energy-dispersive X-ray (EDX) analysis and X-ray analysis.

3. EXPERIMENTAL RESULTS

Interactions occurred between the impurity species in the controlled-impurity helium and the alloys to varying degrees for all test alloys and exposure times. These interactions were manifested by the formation of both surface and internal oxides and carbides, the formation of near-surface denuded zones where alloying element depletion was observed, and near-surface intergranular and intragranular carbide precipitation (carburization). To the extent that these reactions occurred, the test specimens exhibited variations in surface discoloration, scale formation, changes in weight, and changes in carbon concentration.

3.1. WEIGHT CHANGE

Weight change measurements, taken periodically throughout the controlled-impurity helium exposure, serve as a means to monitor the corrosion behavior of the test specimens. In all cases the weight changes were normalized with respect to the individual specimen surface areas. Figures 18 through 24 show the weight change data as a function of exposure time for the present tests.

With the exception of MA 754, all alloys displayed positive weight changes, which tended to increase with increasing exposure time. Occasionally an abrupt weight loss was observed, particularly in the case of pre-oxidized specimens. These weight losses are associated with spallation of the oxide scales upon thermal cycling of the specimens when tests were interrupted to obtain data. Generally speaking, parabolic corrosion rates were observed for those alloys that displayed positive weight changes. In all cases, positive weight changes resulted from either oxidation or a combination of oxidation and carburization.

Fig. 18. Weight change as a function of exposure time for Alloy 800H exposed at 900°C. in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 19. Weight change as a function of exposure time for Hastelloy X exposed at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 20. Weight change as a function of exposure time for Inconel 617 exposed at 900°C in controlled-impurity helium containing 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / $<0.5 \mu\text{atm H}_2\text{O}$

Fig. 21. Weight change as a function of exposure time for IN 100 exposed at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 22.. Weight change as a function of exposure time for IN 713LC exposed at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 23. Weight change as a function of exposure time for HK 40 exposed at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 24. Weight change as a function of exposure time for MA 754 exposed at 900°C in controlled-impurity helium containing $500 \mu\text{atm H}_2/50 \mu\text{atm CO}/50 \mu\text{atm CH}_4/<0.5 \mu\text{atm H}_2\text{O}$

In Figs. 18 through 21 it is interesting to note that for the wrought high-temperature alloys the magnitude of the weight gain with increasing exposure time was consistently lowest for those specimens that were given the preoxidation treatments prior to the controlled-impurity helium exposures. This was not the case, however, for the remainder of the alloys tested. Also important is the fact that for the wrought alloys, the weight gains leveled off almost completely after the 3000-h exposure, which is an indication that the interactions had decreased and the scales formed had limited the kinetics of further gas-metal interactions.

MA 754 exhibited negative weight changes as a function of exposure time independent of surface condition (Fig. 24). This particular alloy has been observed to decarburize in previous experiments in controlled-impurity helium exposures (Ref. 5). It can be assumed that the carbon loss overshadowed any weight increase associated with the formation of an oxide film.

3.2. PREOXIDATION SCALE FORMATION

The preoxidized surface scales were shown in Figs. 13 through 16. Cross sections of the preoxidized specimens were prepared metallographically and the preoxidized scales were studied to more fully characterize the effects of the preoxidation treatments.

Figures 25 through 31 show the oxide scales formed on the test alloys upon preoxidation at 900°C in air. From Figs. 25 and 26, the oxides formed on Alloy 800H and Hastelloy X tended to be thin, continuous, and tenacious. Evidence of substantial internal oxidation can be noted for the longer preoxidation times, particularly for Alloy 800H. In Alloy 800H, alumina scales formed along grain boundaries and extended inward from the outer scales. By X-ray analysis, the outer surface scales were determined to be essentially Cr_2O_3 . Below these scales the oxidation potential decreases dramatically as the distance from the exposed surface increases. Generally, below the surface scale the oxygen activity has decreased to a point where chromium can no longer oxidize. Other more

Fig. 25. Surface oxide scales formed on Alloy 800H specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and (c) 100 h

Fig. 26. Surface oxide scales formed on Hastelloy X specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and 100 h

Fig. 27. Surface oxide scales formed on Inconel 617 specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and (c) 100 h

(a)

(b)

(c)

20 μm

Fig. 28. Surface oxide scales formed on IN 100 specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and (c) 100 h

Fig. 29. Surface oxide scales formed on IN 713LC specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and (c) 100 h

(a)

(b)

(c)

20 μm

Fig. 30. Surface oxide scales formed on HK 40 specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and (c) 100 h

Fig. 31. Surface oxide scales formed on MA 754 specimens during preoxidation treatments at 900°C in air for (a) 1 h, (b) 10 h, and (c) 100 h

reactive chemical constituents, such as silicon or aluminum, can still form oxides under the conditions of low-oxidation potential, and intruding grain-boundary internal oxides resulted.

For the other wrought alloy, Inconel 617, the chromium-rich surface oxide was less continuous, as shown in Fig. 27. Although little evidence of scale spallation was observed (see also Fig. 20), the lack of continuity of the scale would limit its effectiveness as a barrier to carburization in subsequent HTGR-GT environmental exposures. Again, internal oxidation was observed, which increased in severity as the preoxidation time increased.

Figures 28 and 29 show the stages of oxide formation as a function of preoxidation time at 900°C for IN 100 and IN 713LC, the two cast superalloys. Both alloys formed discontinuous oxides during an exposure time of 1 h (Figs. 28a and 29a), and the scale characteristics were similar for both alloys. With longer exposure times, scale formation characteristics became markedly different. Scale evolution in IN 100 became complex, and thick deeply penetrating internal oxides formed (Figs. 28b and 28c). For the case of IN 713LC, more continuous oxide scales formed with the extent of oxidation, i.e., oxidation rate, apparently leveling off between exposure times of 10 and 100 h. There was no indication that the oxidation rate of IN 100 decreased substantially with increasing exposure time.

As mentioned before, the oxidation of HK 40 proceeded through several stages, which are apparent in Fig. 30. The scales formed were discontinuous and the nature of the oxidation behavior seemed to be strongly linked with the orientation of the surface grains. No internal oxidation was observed. Spallation of the surface oxides occurred readily and, in general, the adherence of the oxides appeared to be poor. Spallation of oxide scales formed on HK 40 during controlled-impurity helium exposures has been noted in previous work (Refs. 1-5); however, the utility of this alloy is associated with its ability to resist carburization in severe environmental

exposures (Ref. 16). The scales formed during preoxidation treatments would seemingly have little effect in promoting carburization resistance unless the adherence qualities could be improved.

Finally, from Fig. 31, the oxide scale formed on MA 754 during preoxidation was very thin and contained oxide nodules corresponding to areas of preferential oxidation at yttria particle/alloy matrix interfaces. Similar physical characteristics have been noted in previous oxidation studies (Ref. 18), as well as studies involving corrosion in simulated gas-cooled reactor environments (Ref. 5).

3.3. OXIDATION AND SCALE FORMATION

It was not the purpose of these experiments to perform detailed studies of the reaction products. The interactions of the environment studied in these experiments ($\text{He}/500 \mu\text{atm H}_2/50 \mu\text{atm CO}/50 \mu\text{atm CH}_4/<0.5 \mu\text{atm H}_2\text{O}$) and of similar simulated advanced HTGR environments with the alloys have been extensively studied and reported in past publications (Refs. 1-5). Nonetheless, it was important to compare the surface scales, internal oxidation, and carburization of the specimens to discern any pronounced effects of surface condition. More detailed scale analyses are given in Refs. 1-5.

Figures 32 through 34 show the surface scales that formed on the wrought high-temperature alloys during the controlled-impurity helium exposure. Morphologically the scales are quite similar, independent of surface treatment. Preoxidation treatments resulted in a greater degree of internal oxidation, as might be expected. The surface scales were generally mixed oxides and carbides, although the preoxidized specimens of Alloy 800H and Hastelloy X appeared to contain few carbides but more matrix material within the surface oxide(s). The scale evolution for these alloys is similar to that observed in previous studies (Refs. 4,5).

Fig. 32. Surface scales formed on Alloy 800H specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Specimens were in the following conditions prior to exposure: preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) grit-blasted; (e) lapped; and (f) pickled.

Fig. 33. Surface scales formed on Hastelloy X specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Specimens were in the following conditions prior to exposure: preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) grit-blasted; (e) lapped; and (f) pickled.

Fig. 34. Surface scales formed on Inconel 617 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Specimens were in the following conditions prior to exposure; preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) grit-blasted; (e) lapped; and (f) pickled.

Figures 35 and 36 show the surface scales formed on IN 100 and IN 713LC. From Fig. 35, preoxidation promoted the internal oxidation of IN 100 during the controlled-impurity helium exposure. The grit-blasted and lapped specimens of IN 100 formed thin protective oxide scales in agreement with grit-blasted specimens studied in other simulated reactor exposure experiments (Refs. 1-5). Comparison of Figs. 29 and 36 shows that internal oxidation of the preoxidized IN 713LC specimens occurred during the controlled-impurity helium exposure. The final evolution of surface corrosion products on IN 713LC was similar for all cases of surface treatment.

Figure 37 shows that for HK 40 preoxidation treatments enhanced the internal oxidation susceptibility. Figure 31 shows little if any evidence of internal oxidation following the preoxidation treatments; therefore, all internal oxidation occurred during the controlled-impurity helium exposure. Again, scale formation was complex in all cases and consisted of duplex and triplex scales composed of oxides and carbides, independent of surface finish.

Very thin scales formed on MA 754, as shown in Fig. 38. Preoxidation treatments resulted in the formation of a slightly thicker oxide surface layer, but in general, scale characteristics were similar in all cases.

3.4. CARBURIZATION

Differential interference contrast techniques were employed to study the microstructural aspects of carburization during the controlled-impurity helium exposures. The ingress of carbon results in the intergranular and intragranular precipitation of carbides in a zone near the surface and extending into the specimen to a depth that is a function of exposure time, temperature, environment, alloy chemistry, and surface finish (Refs. 1-5, 11).

Fig. 35. Surface scales formed on IN 100 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Specimens were in the following conditions prior to exposure: preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) grit-blasted; and (e) pickled.

Fig. 36. Surface scales formed on IN 713LC specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / $<0.5 \mu\text{atm H}_2\text{O}$. Specimens were in the following conditions prior to exposure: preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) grit-blasted; and (e) lapped.

(a)

(d)

(b)

(e)

(c)

20 μm

Fig. 37. Surface scales formed on HK 40 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO/50 μatm CH_4 / <0.5 μatm H_2O . Specimens were in the following conditions prior to exposure: preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) grit-blasted; and (e) lapped.

Fig. 38. Surface scales formed on MA 754 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Specimens were in the following conditions prior to exposure: preoxidized in air for (a) 1 h, (b) 10 h, and (c) 100 h; (d) lapped; and (e) pickled.

In Fig. 39 a comparison is made between Alloy 800H specimens given a preoxidation treatment and those given a pickling treatment. Figure 39a is typical of the microstructures observed for the preoxidized specimens. Thermal aging, which has occurred, resulted in the formation of generally discontinuous grain-boundary networks of $M_{23}C_6$ (Ref. 12). The pickled specimen, shown in Fig. 39a, contained grain-boundary carbide networks, which appeared to be more continuous than in the preoxidized specimen, and also showed an increase in the density of intragranular carbides.

These intragranular carbides sometimes appeared as Widmännstätten precipitates with very clearly defined habit planes. In the case of the pickled, grit-blasted, or lapped specimens, twin boundaries were decorated with carbides to a greater extent than in those specimens given preoxidation treatments. Metallographically, it is more difficult to establish carburization depths in Alloy 800H since carburization results primarily in the intergranular precipitation of $M_{23}C_6$ carbides, as does thermal aging reactions at 900°C (Refs. 1-5, 12). It is therefore more difficult to distinguish between thermal aging effects and enhanced precipitation as a result of carburization.

In the case of Hastelloy X, the thermal aging reactions result in the precipitation of M_6C carbides, whereas carburization results in the precipitation of $M_{23}C_6$ -type carbides. The inherent hardness differences, leading to differences in "relief" for polished specimens, make a technique such as differential interference contrast invaluable in interpreting and distinguishing carburization effects. Figure 40b shows an example of carburization in Hastelloy X. In Fig. 40a no carburization was observed in the specimen preoxidized 10 h. This was typical of the specimens preoxidized 1 and 100 h as well. Carburization, morphologically similar to that observed in Fig. 40b, occurred in the lapped and grit-blasted specimens also.

Figure 41 shows examples of carburization observed for Inconel 617. Although the specimen in Fig. 41a was preoxidized, little apparent benefit was gained with respect to inhibiting carbon ingress. A slightly lower

Fig. 39. Differential interference contrast photomicrographs showing Alloy 800H specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO/50 μatm CH_4 / <0.5 μatm H_2O . Prior to exposure surface condition was (a) preoxidized 10 h and (b) pickled.

Fig. 40. Differential interference contrast photomicrographs showing Hastelloy X specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Prior to exposure specimen surface condition was (a) preoxidized 10 h and (b) pickled.

Fig. 41. Differential interference contrast photomicrographs showing Inconel 617 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Prior to exposure surface condition was (a) preoxidized 100 h and (b) pickled.

intragranular carbide density was observed in the carburized zone for the preoxidized specimens as compared to the lapped, grit-blasted, or pickled specimens. This behavior can probably be attributed to the preoxidized scales being somewhat effective barriers, but the discontinuity of the scales still permitted some carbon ingress.

Interestingly enough, preoxidation treatments seemed to increase the severity of carburization for the cast superalloys. The preoxidized specimens of IN 100 and IN 713LC (Figs. 42 and 43) showed increased carbide densities and more continuous intergranular carbide networks than those observed for either lapped or grit-blasted specimens (lapped specimens are shown).

Figure 44 shows differential interference contrast photographs typical of those observed for HK 40 and MA 754, independent of surface condition. The high carbon concentration of HK 40 ($\sim 0.4\%$) leads to difficulty in distinguishing carbide precipitation reactions associated with thermal aging from those associated with carburization. It is apparent from Fig. 44a that the carburized zone in HK 40 had a heavier density of intragranular carbides, although this effect was not consistently observable. In the case of MA 754, decarburization has been observed upon exposure to simulated reactor helium environments (Refs. 4,5); therefore, no morphological effects are associated with carburization.

3.5. BULK CARBON CONTENT ANALYSES

As a means of comparison and to provide insight as to the severity of the carburization phenomenon, bulk carbon concentrations were determined for the post-exposure specimens and for specimens prior to testing. For all the alloys, the change of carbon concentration varied with the particular surface condition. The carbon concentrations as a function of surface condition are shown in Figs. 45 through 51.

Fig. 42. Differential interference contrast photomicrographs showing IN 100 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Prior to exposure specimen condition was (a) preoxidized 100 h and (b) lapped.

Fig. 43. Differential interference contrast photomicrographs showing IN 713LC specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Prior to exposure specimen condition was (a) preoxidized 10 h and (b) lapped.

Fig. 44. Differential interference contrast photomicrographs showing (a) HK 40 and (b) MA 754 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O . Prior to exposure both specimens were preoxidized 10 h.

Fig. 45. Bulk carbon concentrations for Alloy 800H specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / $<0.5 \mu\text{atm H}_2\text{O}$

Fig. 46. Bulk carbon concentrations for Hastelloy X specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 47. Bulk carbon concentrations for Inconel 617 specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 48. Bulk carbon concentrations for IN 100 specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / <0.5 $\mu\text{atm H}_2\text{O}$

Fig. 49. Bulk carbon concentrations for IN 713LC specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / <0.5 $\mu\text{atm H}_2\text{O}$

Fig. 50. Bulk carbon concentrations for HK 40 specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 $\mu\text{atm H}_2$ /50 $\mu\text{atm CO}$ /50 $\mu\text{atm CH}_4$ / <0.5 $\mu\text{atm H}_2\text{O}$

Fig. 51. Bulk carbon concentrations for MA 754 specimens following exposure for 3000 h at 900°C to controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

It is clear from Figs. 45 through 47 that preoxidation treatments were effective in controlling carburization for Alloy 800H and Hastelloy X and partially effective in the case of Inconel 617. For the latter alloy, longer-term preoxidation treatments were less effective than the short-term 1-h treatment. No consistent observations along these lines could be made for the other wrought alloys, which exhibited only modest increases in carbon concentrations (if any) for all preoxidized specimens. Aside from preoxidation, the other surface treatments had little effect on the subsequent carburization of the wrought high-temperature alloys in controlled-impurity helium.

Figure 48 shows the carbon concentrations measured for IN 100. In sharp contrast to the wrought alloys, carburization was more pronounced in specimens given prior preoxidation treatments. The lapped and grit-blasted specimens showed virtually no change in carbon content following the controlled-impurity helium exposure. The resistance of IN 100 to carburization in simulated reactor helium environments has been noted in previous studies (Refs. 1-5).

In Fig. 49, the results indicate that surface finish has little effect on the carburization behavior of IN 713LC. As with IN 100, preoxidation treatments did not inhibit carburization. It has been previously reported that IN 713LC is not as effective as IN 100 in resisting carburization (Refs. 4, 5); Figs. 48 and 49 would appear to confirm the earlier observations.

Figure 50 shows the bulk carbon data for HK 40. The driving force for carburization (relative to the initial carbon concentration) to occur is drastically reduced by the large initial carbon concentration of HK 40. These data would indicate that surface finish plays only a minor role, of secondary importance, in the susceptibility of this alloy to carburization in controlled-impurity helium environments.

The unique situation of MA 754 is clearly shown in Fig. 51. In contrast to the other alloys tested, the phenomenon of decarburization

occurred upon exposure to a simulated reactor helium environment. Decarburization of MA 754 has been associated with the yttria dispersoids and the possibility that the yttria/matrix interface acts as a favorable surface for the oxidation of matrix carbon (Ref. 5). Again, these experiments did not indicate that surface finish had an important effect on the corrosion behavior of MA 754.

4. DISCUSSION

The effects of surface finish on the controlled-impurity helium corrosion behavior of seven candidate alloys are summarized in Table 3. The important surface corrosion product morphological characteristics observed for the various surface conditions studied are also given in Table 3. The behavior of three alloys, MA 754, HK 40, and IN 713LC, was essentially independent of the initial surface finish. Carburization of alloys HK 40 and IN 713LC was not inhibited by any particular surface condition including preoxidation. The decarburization behavior of MA 754 was also not strongly affected by altering surface condition.

IN 100 and the wrought high-temperature alloys, Alloy 800H, Hastelloy X, and Inconel 617, showed a stronger effect of surface condition on simulated reactor environment performance. Preoxidation treatments were ineffective in controlling the carburization of IN 100 and actually increased carburization susceptibility. Most probably this was related to the oxide that formed in the preoxidation exposure. IN 100 has been shown to be resistant to carburization in previous simulated reactor helium corrosion studies (Refs. 1-5) and this behavior was related to the formation of a thin, continuous, adherent, aluminum-rich oxide scale (Refs. 4,5). Carburization resistance was enhanced when this alumina scale contained small but measureable amounts of titanium.

When exposed to air, the oxidation behavior is likely to be much different, and the evolution of chromium-aluminum-based oxides was observed. Mixed oxides and chromium-based oxides, formed during controlled-impurity helium exposures, have been shown to be generally ineffective in controlling carburization in most alloys (Refs. 1-5). Previous studies have shown that oxidation of IN 100 at 760° to 1100°C in air does not produce

TABLE 3
CORROSION BEHAVIOR AFTER 3000-HOUR EXPOSURES TO A CONTROLLED-IMPURITY HELIUM ENVIRONMENT

Alloy	Surface Condition	Surface Scale Thickness (μm)	Depth of Internal Oxidation (μm)	Depth of Alloying Element Depleted Zone (μm)	Carburized Zone Penetration Depth (μm)
Alloy 800H	Preoxidized 1 h	13	41	70	--
	Preoxidized 10 h	14	44	89	--
	Preoxidized 100 h	13	44	89	--
	Grit-blasted	10	76	76	680
	Lapped	10	29	51	735
	Pickled	11	32	38	815
Hastelloy X	Preoxidized 1 h	10	29	29	--
	Preoxidized 10 h	8	25	25	--
	Preoxidized 100 h	8	25	25	--
	Grit-blasted	8	25	51	222
	Lapped	8	25	51	222
	Pickled	11	25	51	191
Inconel 617	Preoxidized 1 h	8	32	70	308
	Preoxidized 10 h	8	32	70	381
	Preoxidized 100 h	8	38	70	254
	Grit-blasted	8	38	64	572
	Lapped	6	25	51	381
	Pickled	8	44	67	635
IN 100	Preoxidized 1 h	4	32	44	--
	Preoxidized 10 h	13	41	70	191
	Preoxidized 100 h	60	70	108	445
	Grit-blasted	6	6	38	76
	Lapped	10	10	38	89
IN 713LC	Preoxidized 1 h	4	41	57	572
	Preoxidized 10 h	6	51	70	572
	Preoxidized 100 h	10	38	64	572
	Grit-blasted	6	32	51	318
	Lapped	10	38	57	635
HK 40	Preoxidized 1 h	10	19	25	403
	Preoxidized 10 h	11	29	32	410
	Preoxidized 100 h	10	25	25	590
	Grit-blasted	11	29	32	508
	Lapped	8	22	22	572
MA 754	Preoxidized 1 h	4	--	--	--
	Preoxidized 10 h	3	--	--	--
	Preoxidized 100 h	3	--	--	--
	Lapped	4	--	--	--
	Pickled	4	--	--	--

Al_2O_3 as the steady-state scale (Ref. 19). The establishment of a (Ni,Co)O surface oxide layer containing large proportions of TiO_2 as an initial scale is caused by surface chemical inhomogeneities. The low, but still adequate, oxygen potential beneath this scale causes aluminum to be internally oxidized, as was observed in Fig. 35. Rapid oxidation continues and the surface scale that eventually evolves [(Ni,Co)O containing NiTiO_3] has a defect structure such that carbon ingress can continue unabated while a scale more stable in HTGR helium forms. In the cases of the grit-blasted and lapped IN 100 specimens, alumina scales containing titanium, which naturally formed during the controlled-impurity helium exposure, significantly inhibited carburization. This behavior contrasts well with that of IN 713LC, where alumina scales could still form (except in the preoxidized specimens), but the low titanium concentration of IN 713LC limited the ability to incorporate titanium into the alumina scale; the scale thus formed was not as effective as a carburization barrier. These observations are consistent with previous studies that outlined the importance of aluminum-based oxides in carburization control (Refs. 4, 5).

The effectiveness of preoxidized surface scales in inhibiting the carburization of the wrought high-temperature alloys revealed many important features of the corrosion behavior of wrought alloys in simulated reactor helium. The formation of preoxidized surface scales virtually eliminated carburization for the two wrought alloys, Alloy 800H and Hastelloy X, while decreasing the severity of carburization for Inconel 617.

Attention was focused on the scale characteristics pertaining to Alloy 800H and Hastelloy X. Figures 52 through 54 show the surface scales of preoxidized Alloy 800H in the preoxidized condition and following the controlled-impurity helium exposures. As preoxidation time increased, the thickness of the oxide scale formed during preoxidation increased, as would be expected. The same can be stated for the preoxidation behavior of Hastelloy X, shown in Figs. 55 through 57. Interestingly enough, the thicknesses of the surface oxide scales following the

Fig. 52. Scanning electron micrographs showing surface scales formed on Alloy 800H: (a) preoxidized at 900°C in air for 1 h and (b) preoxidized in air for 1 h and exposed for 3000 h in He/500 μatm H_2 /50 μatm CO/50 μatm CH_4 / <0.5 μatm H_2O at 900°C. Arrow in (a) indicates oxide scale.

(a)

(b)

20 μm

Fig. 53. Scanning electron micrographs showing surface scales formed on Alloy 800H: (a) preoxidized at 900°C in air for 10 h and (b) preoxidized in air for 10 h and exposed for 3000 h in He/500 μatm H_2 /50 μatm CO/50 μatm CH_4 / <0.5 μatm H_2O at 900°C

(a)

(b)

20 μm

Fig. 54. Scanning electron micrographs showing surface scales formed on Alloy 800H: (a) preoxidized at 900°C in air for 100 h and (b) preoxidized in air for 100 h and exposed for 3000 h in He/500 μatm H₂/50 μatm CO/50 μatm CH₄/ <0.5 μatm H₂O at 900°C

(a)

10 μm

(b)

20 μm

Fig. 55. Scanning electron micrographs showing surface scales formed on Hastelloy X: (a) preoxidized at 900°C in air for 1 h and (b) preoxidized in air for 1 h and exposed for 3000 h in He/500 μatm H_2 /50 μatm CO/50 μatm CH_4 / <0.5 μatm H_2O at 900°C. Arrow in (a) indicates oxide scale.

(a)

(b)

20 μm

Fig. 56. Scanning electron micrographs showing surface scales formed on Hastelloy X: (a) preoxidized at 900°C in air for 10 h and (b) preoxidized in air for 10 h and exposed for 3000 h in He/500 μatm H₂/50 μatm CO/50 μatm CH₄/ <0.5 μatm H₂O at 900°C. Arrow in (a) indicates oxide scale.

(a)

(b)

20 μm

Fig. 57. Scanning electron micrographs showing surface scales formed on Hastelloy X: (a) preoxidized at 900°C in air for 100 h and (b) preoxidized in air for 100 h and exposed for 3000 h in He/500 μatm H₂/50 μatm CO/50 μatm CH₄/ <0.5 μatm H₂O at 900°C.

controlled-impurity helium exposures were a function of alloy chemistry but were independent of initial preoxidized scale thickness. (It should be noted that whitish areas on the outer edge of the surface scales are silver nodules. Silver was deposited on the specimens prior to the electrodeposition of nickel to promote adhesion of the nickel. This procedure was followed to maintain good edge retention of the specimens. Despite these efforts, examples where the oxide has separated from the protective nickel layer were observed. In Fig. 51a, for example, diamond paste polishing compound particles have become embedded in between the oxide and the mounting resin.)

Table 4 shows the concentrations of metallic elements found in the oxide surface layers, in both the preoxidized and the post-HTGR-GT exposure conditions for Alloy 800H and Hastelloy X. After 1-h preoxidation treatments, the scales for both alloys were chromium-rich but contained substantial proportions of other metallic elements. These scales were very thin and therefore difficult to analyze without matrix "shine" and interference. Although initial stages of oxide formation in these alloys are complex and involve the formation of oxide phases of intermediate stability (Ref. 18), the longer-term preoxidation treatments led to the formation of Cr_2O_3 scales for both alloys with only trace quantities of other metallic elements.

Following the controlled-impurity helium exposure, the protective oxide scales were found to contain substantial proportions of manganese. In the case of Alloy 800H, manganese concentrations on the order of one-third to one-half the concentrations of chromium were observed. The composition of the scales on Alloy 800H was uniform, indicating that a metastable steady-state situation had probably developed. For Hastelloy X, only the scale of the 1-h preoxidized specimen had manganese concentrations in proportion to those observed for Alloy 800H. Those Hastelloy X specimens that had been given 10 or 100 h preoxidation treatments had lower manganese concentrations in the oxide scales. Some Japanese studies (Refs. 20, 21) have shown manganese to be beneficial in inhibiting

TABLE 4
CONCENTRATIONS OF METALLIC ELEMENTS OBSERVED IN OXIDE SURFACE SCALES FORMED ON
HASTELLOY X AND ALLOY 800H FOR PREOXIDIZED AND HTGR-GT EXPOSURE CONDITIONS

Alloy	Condition	Concentration of Metallic Elements in Surface Oxide Scale (wt %)
Alloy 800H	Preoxidized in air for 1 h at 900°C	68 Cr, 11 Ni, 10 Fe, 4.3 Mn, 3.6 Al, 1.6 Ti, 0.6 Si
	Preoxidized in air for 10 h at 900°C	98 Cr, 1 Ti, 0.7 Mn, 0.3 Si
	Preoxidized in air for 100 h at 900°C	98 Cr, 0.8 Ti, 0.8 Mn, 0.1 Fe
	Preoxidized 1 h + 3000 h in controlled-impurity He	67 Cr, 28 Mn, 2.5 Ti, 0.7 Al, 0.6 Si, 0.6 Ni
	Preoxidized 10 h + 3000 h in controlled-impurity He	70 Cr, 25 Mn, 3 Ti, 1 Al, 1 Si, 0.3 Fe
	Preoxidized 100 h + 3000 h in controlled-impurity He	68 Cr, 28 Mn, 2.8 Ti, 0.5 Fe, 0.2 Al
Hastelloy X	Preoxidized in air for 1 h at 900°C	82 Cr, 6.5 Ni, 4.7 Mo, 4 Fe, 1.4 Si, 1.2 Mn, 0.1 Co
	Preoxidized in air for 10 h at 900°C	97.8 Cr, 1 Mn, 0.6 Ni, 0.3 Si, 0.1 Mo, 0.1 Fe
	Preoxidized in air for 100 h at 900°C	98 Cr, 0.6 Mo, 0.5 Fe, 0.3 Mn, 0.3 Si, 0.2 Ni
	Preoxidized 1 h + 3000 h in controlled-impurity He	73 Cr, 24 Mn, 1.3 Si, 0.7 Fe, 0.6 Ni
	Preoxidized 10 h + 3000 h in controlled-impurity He	85 Cr, 14 Mn, 0.5 Si
	Preoxidized 100 h + 3000 h in controlled-impurity He	82 Cr, 12 Mn, 3 Mo, 3 Si

corrosion and oxide spallation of Hastelloy X in simulated reactor helium environments by forming a Cr_2MnO_4 spinel. X-ray studies of the post-exposed surface scales of the preoxidized specimens (Alloy 800H and Hastelloy X) showed that the Alloy 800H surface oxides were $\sim\text{Cr}_2\text{MnO}_4$ spinels with a lattice parameter $a_0 \approx 8.52 \text{ \AA}$, while the Hastelloy X surface scales were a mixture of a Cr_2MnO_4 spinel, with a lattice parameter of $\approx 8.49 \text{ \AA}$, and Cr_2O_3 . Obviously, the scales on the surface of the Hastelloy X specimens were still in a state of transition from Cr_2O_3 to Cr_2MnO_4 ($\text{Cr}_2\text{O}_3 + \text{MnO}$), with the 1-h preoxidized specimen being closest to having completed this transition to a steady-state condition. The compositions of the scales on Alloy 800H and Hastelloy X were shifting to the stoichiometric composition corresponding to Cr_2MnO_4 .

Figures 58 through 64 show the surface scale characteristics following the controlled-impurity helium exposure as a function of preoxidation time for all of the alloys studied. In general, the surface scales that developed on the preoxidized specimens were similar, regardless of preoxidation exposure time. The exception was IN 100, as shown in Fig. 61. Particularly after a 100-h preoxidation treatment, the internal oxidation and surface scale thicknesses extended deeply into the alloy matrix as oxidation continued during the controlled-impurity helium exposure.

The effectiveness of the preoxidation treatments in controlling the controlled-impurity helium carburization behavior of Alloy 800H and Hastelloy X was related to the establishment of a diffusion barrier that prevented carbon ingress. The preoxidized surface scales, essentially Cr_2O_3 , were unstable with respect to the oxygen potential established in the controlled-impurity helium exposure. Cr_2O_3 oxides formed in air, however, did serve as carbon diffusion barriers as the steady-state oxide scales were established. In general, chromium oxides, carbides, or chromium-based duplex and triplex scales formed during controlled-impurity helium exposures are not protective and offer little resistance to continued carburization and/or oxidation (Refs. 1-5). It would appear

Fig. 58. Corrosion characteristics of preoxidized Alloy 800H specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 59. Corrosion characteristics of preoxidized Hastelloy X specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 60. Corrosion characteristics of preoxidized Inconel 617 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O .

Fig. 61. Corrosion characteristics of preoxidized IN 100 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 62. Corrosion characteristics of preoxidized IN 713LC specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 63. Corrosion characteristics of preoxidized HK 40 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

Fig. 64. Corrosion characteristics of preoxidized MA 754 specimens exposed 3000 h at 900°C in controlled-impurity helium containing 500 μatm H_2 /50 μatm CO /50 μatm CH_4 / <0.5 μatm H_2O

that Cr_2O_3 -type oxides, formed in air, have a defect structure that inhibits carbon diffusion. These initial temporary carbon barriers gave way to more stable oxide spinel films, and these steady-state films remained diffusion barriers with respect to carbon ingress.

By making proper utilization of diffusion barriers (directly applied coatings, preoxidized scales, claddings, etc.) it should be possible to control the carburization normally observed for many alloys in simulated reactor helium environments.

5. CONCLUSIONS

The conclusions from the first part of the study on the effects of prior surface condition are as follows:

1. Preoxidation treatments in air at 900°C have been shown to inhibit carburization of Alloy 800H and Hastelloy X for 3000 h in a simulated reactor helium exposure, also at 900°C.
2. Preoxidation treatments in air at 900°C increased the severity of carburization observed for IN 100 in a simulated reactor helium exposure at 900°C, as compared to lapped or grit-blasted surfaces where carburization resistance was adequate.
3. Surface finish had no important effect upon the simulated reactor helium corrosion behavior of alloys HK 40 and MA 754 and only a minor effect upon the corrosion behavior of IN 713LC and Inconel 617.
4. Decarburization was observed for all surface conditions of MA 754 following exposures in a simulated reactor helium environment.
5. Although thermodynamically unstable, oxide scales formed in air can resist the carburization of some alloys during simulated reactor helium exposures. These scales transform to more stable forms of oxide which continue to be carburization barriers.

6. Effective carburization-barrier scales appear to be based upon either the Al_2O_3 oxides containing titanium or spinels similar to Cr_2MnO_4 . The protective nature of these scales is dependent upon the manner in which they are formed. Chromium-manganese oxide scales formed without preoxidation do not necessarily inhibit carburization.

6. RECOMMENDATIONS FOR FUTURE WORK

The following recommendations are made for future research:

1. The experiments performed in this study were of a relatively short duration. Longer-term studies should be initiated to investigate not only long-term exposure stability characteristics of preoxidized scales but also the effects of preoxidation environment, temperature, and time on the performance of alloys in simulated reactor helium environments.
2. The spallation behavior of preoxidized surface scales should be studied with particular emphasis upon thermal cycling and reactor temperature profiles/environments. As a complementary area of study, the "self-healing" characteristics of protective preoxidized scales should be investigated. In addition, the kinetics and microstructural consequences of carburization in areas where spallation has occurred should be determined.
3. The use of Fe-Mn-Cr and Ni-Mn-Cr alloys as cladding/coating materials should be investigated. The manganese and chromium concentrations could be adjusted to the appropriate levels leading to the formation of protective "coatings" based on the Cr_2MnO_4 spinel, either during preoxidation treatments or during actual HTGR-GT environmental exposures.
4. Alloy design projects should be initiated with the objective of developing alloy systems that form protective scales based upon manganese spinels and alumina-based oxides when exposed to simulated reactor helium environments. Adequate mechanical properties for reactor operating conditions must, of course, be maintained in addition to acceptable corrosion behavior.

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